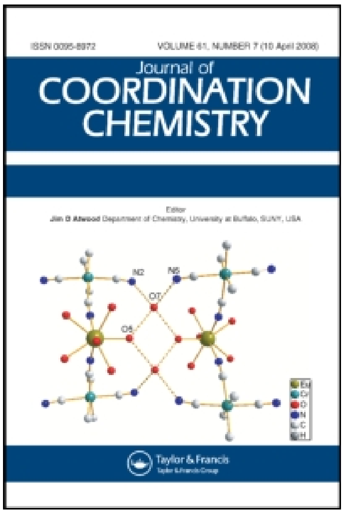

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COMPLEXES OF BUTYLTIN(IV) WITH MONOTHIOACETYLACETONE AND *TERT*-BUTYLTRIFLUOROACETYLACETONE

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COMPLEXES OF BUTYLTIN(IV) WITH MONOTHIOACETYLACETONE AND *TERT*-BUTYLTRIFLUOROACETYLACETONE

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The reaction of butyltin(IV) trichloride with the sodium salt of monothioacetylacetone and *tert*-butyltrifluoroacetylacetone results in formation of monomeric complexes $BuSnCl_{3-n}(MeCSCHCOMe)_n$ and $BuSnCl_{3-n}(CF_3COCHCO^t\text{-}Bu)_n$ (n = 1–3). All the complexes were characterized by elemental analyses, IR, NMR (^1H, ^{13}C, ^{119}Sn, ^{19}F), molar conductance and molecular weight determination. The results show that in all the complexes ligands coordinate to tin(IV) as bidentate donors.

Keywords: butyltin(IV); monothioacetylacetone; *tert*-butyltrifluoroacetylacetone; monomeric; complexes

INTRODUCTION

Metal-β-ketonates[1] have been the subject of renewed interest because they happen to be synthetically accessible and soluble metalloorganic compounds for preparing heterometallic aggregates.[2] The aggregates function as intermediates in sol-gel processes for multicomponent oxides. Also metal chelates derived from unsymmetrical ligands like monothio-β-diketones[3] and fluoro-β-diketones[4] provide excellent systems to probe the origin of novel properties observed in the complexes. With this aim we have under taken a systematic investigation of such complexes.[5-7] Here we report the synthesis and characterization of a few tin(IV) thio- and fluoro-β-diketonates which may find application in the production of solid state materials based on tin.

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EXPERIMENTAL

All experimental manipulations were performed under a dry nitrogen atmosphere. Solvents were dried by standard techniques. Monothioacetylacetone was synthesized by the H_2S method[8] and converted into its sodium salt by literature procedures.[9] *Tert*-butyltrifluoroacetylacetone was synthesized by Claisen-condensation methods[10] and its sodium salt was prepared by the addition of a benzene solution of the ligand to sodium hydride suspension in benzene at 0°C. Butyltin(IV) trichloride was distilled (30°C/10mm) before use.

For analysis tin was estimated as SnO_2; chlorine as silver chloride (gravimetrically); and sulfur was estimated by Messenger's method. Carbon and hydrogen were analyzed microanalytically. Conductivity measurements were performed with a conductometer (L-370873, Cambridge Instruments) at 25°C in acetonitrile at 10^{-3}M concentration. IR spectra (as nujol mulls) were recorded on a Perkin-Elmer 621 spectrophotometer using CsI plates. NMR spectra were recorded on a JEOL FX 90 Q spectrometer in $CDCl_3$ (TMS was an internal standard for ^1H and ^{13}C, $CFCl_3$ for ^{19}F and tetramethyltin was an external reference for ^{119}Sn).

General procedure for the synthesis of butyltin(IV) complexes with monothioacetylacetone, $BuSnCl_{3-n}(MeCSCHCOMe)_n$ $(n = 1-3)$

A solution of butyltin(IV) trichloride in dichloromethane (20 mL) was added dropwise to a stirring suspension of the sodium salt of monothioacetylacetone (30 mL) at 0°C. The stoichiometries taken were 1:1, 1:2 and 1:3 for $BuSnCl_2(MeCSCHCOMe)$, $BuSnCl(MeCSCHCOMe)_2$ and $BuSn(MeCSCHCOMe)_3$, respectively. The bath temperature was allowed to rise to room temperature and the reaction mixture was stirred for 4h. The solution was then filtered to remove sodium chloride and washed with dichloromethane (10 mL). Solvent was removed from the filtrate at reduced pressure. The isolated product was dried at 0.1mm/4h/25°C. Yields were about 95%.

$BuSnCl_2(MeCSCHCOMe)$.

Anal. Calcd. for $C_9H_{16}Cl_2OSSn$(%): C, 29.85; H, 4.42; S, 8.84; Sn, 32.81. Found: C, 29.75; H, 4.40; S, 8.68; Sn, 32.65. IR: ν(C=O) 1600(s); ν(C=C) 1500(s); ν(C=S) 1220(s); ν(C=S) + δ(C-H) 820(m); ν(Sn-C) 500(s); ν(Sn-O) 468(s); ν(Sn-S) 390(s); ν(Sn-Cl) 342(s), 290(m). ^1H NMR ($CDCl_3$): δ 0.85(t, 3H, CH_3); 1.45(m, 6H, $(CH_2)_3$); 2.24 (s, 3H, CS-CH_3); 2.28(s, 3H, CO-CH_3); 6.44(s, 1H, CH). ^{13}C NMR ($CDCl_3$): ppm 13.10, 26.22, 28.00, 28.52, 32.34, 34.70, 119.72, 172.81 (CO), 202.39 (CS). ^{119}Sn NMR ($CDCl_3$): ppm −130. Conductivity: 0.02 Ohm^{-1} cm^{2}mol^{-1}. Molecular weight: Calcd. for $C_9H_{16}Cl_2OSSn$: 361.69; Found: 367.

BuSnCl(MeCSCHCOMe)$_2$

Anal. Calcd. for $C_{14}H_{23}ClO_2S_2Sn$(%): C, 38.07; H, 5.21; S, 14.50; Sn, 26.90. Found: C, 37.90; H, 5.19; S, 14.31; Sn, 26.92. IR: ν(C=O) 1590(s); ν(C=C) 1495(s); ν(C=S) 1222(s); ν(C=S) + δ(C-H) 812(m); ν(Sn-C) 502(s); ν(Sn-O) 470(s); ν(Sn-S) 362(s); ν(Sn-Cl) 292(s). ^{1}H NMR ($CDCl_3$): δ 0.82(t, 3H, CH_3); 1.40(m, 6H, $(CH_2)_3$); 2.21 (s, 6H, CS-CH_3); 2.30(s, 6H, CO-CH_3); 6.45(s, 2H, CH). ^{13}C NMR ($CDCl_3$): ppm 13.00, 26.20, 28.20, 28.42, 33.10, 38.14, 118.16, 180.00 (CO), 199.38 (CS). ^{119}Sn NMR ($CDCl_3$): ppm −235. Conductivity: 0.01 Ohm^{-1} cm^{2}mol^{-1}. Molecular weight: Calcd. for $C_{14}H_{23}ClO_2S_2Sn$: 441.19; Found: 436.

BuSn(MeCSCHCOMe)$_3$

Anal. Calcd. for $C_{19}H_{30}O_3S_3Sn$(%): C, 43.78; H, 5.76; S, 18.43; Sn, 22.79. Found: C, 43.70; H, 5.72; S, 18.36; Sn, 22.58. IR: ν(C=O) 1605(s); ν(C=C) 1500(s); ν(C=S) 1220(s); ν(C=S) + δ(C-H) 810(m); ν(Sn-C) 501(s); ν(Sn-O) 469(s); ν(Sn-S) 370(s). ^{1}H NMR ($CDCl_3$): δ 0.83(t, 3H, CH_3); 1.42(m, 6H, $(CH_2)_3$); 2.20 (s, 9H, CS-CH_3); 2.25(s, 9H, CO-CH_3); 6.40(s, 3H, CH). ^{13}C NMR ($CDCl_3$): ppm 13.12, 26.20, 28.02, 28.50, 33.18, 34.92, 120.62, 173.72 (CO), 201.86 (CS). Conductivity: 0.00 Ohm^{-1} cm^{2}mol^{-1}. Molecular weight: Calcd. for $C_{19}H_{30}O_3S_3Sn$: 520.69; Found: 516.

General procedure for the synthesis of butyltin(IV) complexes with tert-butyltrifluoroacetylacetone, $BuSnCl_{3-n}(CF_3COCHCO^t\text{-}Bu)_n$ ($n = 1-3$)

Butyltin(IV) trichloride dissolved in benzene (15 mL) was added dropwise to a stirring suspension of the sodium salt of *tert*-butyltrifluoroacetylacetone in benzene (35 mL) at room temperature. Reactants were taken in 1:1, 1:2 and 1:3 molar ratio for $BuSnCl_2(CF_3COCHO^t\text{-}Bu)$, $BuSnCl(CF_3COCHCO^t\text{-}Bu)_2$ and $BuSn(CF_3COCHCO^t\text{-}Bu)_3$, respectively. The reaction mixture was stirred at room temperature for 5h; sodium chloride separated was removed by filtration. Solvent was removed from the filtrate at reduced pressure and the products were dried at 0.1mm/4h/35°C. Yields were about 94%.

$BuSnCl_2(CF_3COCHCO^t\text{-}Bu)$

Anal. Calcd. for $C_{12}H_{19}Cl_2F_3O_2Sn$(%): C, 32.60; H, 4.30; Cl, 16.07; Sn, 26.87. Found: C, 32.52; H, 4.34; Cl, 16.14; Sn, 26.80. IR: ν(C=O) 1610(s); ν(C=C) 1524(s); ν(Sn-C) 583(s); ν(Sn-O) 424(s); ν(Sn-Cl) 340(s), 210(m). ^{1}H NMR ($CDCl_3$): δ 0.87(t, 3H, CH_3); 1.52(m, 6H, $(CH_2)_3$); 2.30(s, 9H, t-C_4H_9); 6.00(s, 1H, CH). ^{13}C NMR ($CDCl_3$): ppm 14.00, 26.52, 28.30, 28.75, 31.10, 123.51, 127.40, 170.50, 201.10. ^{19}F NMR ($CDCl_3$): ppm 70.5. ^{119}Sn NMR ($CDCl_3$): ppm −133.5. Conductivity: 0.01 Ohm^{-1} cm^{2}mol^{-1}. Molecular weight: Calcd. for $C_{12}H_{19}Cl_2F_3O_2Sn$: 441.69; Found: 434.

$BuSnCl(CF_3COCHCO^t\text{-}Bu)_2$

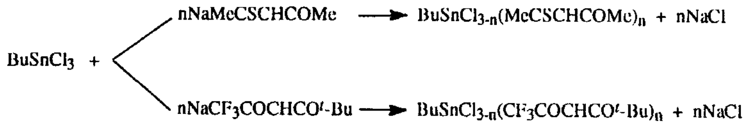
Anal. Calcd. for $C_{20}H_{29}ClF_6O_4Sn$(%): C, 39.92; H, 4.82;, Cl, 5.90; Sn, 19.74. Found: C, 39.81; H, 4.80; Cl, 5.78; Sn, 19.66. IR: ν(C=O) 1600(s); ν(C=C) 1525(s); ν(Sn-C) 580(s); ν(Sn-O) 422(s); ν(Sn-Cl) 262(m). ^{1}H NMR ($CDCl_3$): δ 0.85(t, 3H, CH_3); 1.50(m, 6H, $(CH_2)_3$); 2.33 (s, 18H, t-C_4H_9); 5.94(s, 2H, CH). ^{13}C NMR ($CDCl_3$): ppm 14.10, 26.42, 28.10, 28.70, 33.05, 118.72, 131.10, 172.40, 202.00. ^{19}F NMR ($CDCl_3$): ppm 74.0. ^{119}Sn NMR ($CDCl_3$): ppm −230. Conductivity: 0.01 Ohm^{-1} cm^{2}mol^{-1}. Molecular weight: Calcd. for $C_{20}H_{29}ClF_6O_4Sn$: 601.19; Found: 594.

$BuSn(CF_3COCHCO^t\text{-}Bu)_3$

Anal. Calcd. for $C_{28}H_{39}F_9O_6Sn$(%): C, 44.17; H, 5.12, Sn, 15.60. Found: C, 44.06; H, 5.10; Sn, 15.50. IR: ν(C=O) 1602(s); ν(C=C) 1522(s); ν(Sn-C) 581(s); ν(Sn-O) 422(s). ^{1}H NMR ($CDCl_3$): δ 0.82(t, 3H, CH_3); 1.49(m, 6H, $(CH_2)_3$); 2.32 (s, 27H, t-C_4H_9); 5.59(s, 3H, CH). ^{13}C NMR ($CDCl_3$): ppm 14.20, 26.50, 28.20, 28.65, 31.00, 124.00, 127.20, 171.20, 202..30. Conductivity: 0.00 Ohm^{-1} cm^{2}mol^{-1}. Molecular weight: Calcd. for $C_{28}H_{39}F_9O_6Sn$: 760.69; Found: 751.

RESULTS AND DISCUSSION

Complexes of butyltin(IV) with monothioacetylacetone and *tert*-butyltrifluoroacetylacetone have been synthesized by the following reaction routes:



(n = 1-3)

All the complexes of butyltin(IV) with monothioacetylacetone and *tert*-butyltrifluoroacetylacetone are liquid except $BuSn(MeCSCHCOMe)_3$ which is low melting solid, soluble in common organic solvents. They are monomeric in benzene as found cryoscopically.

IR spectra of $BuSnCl_{3-n}(MeCSCHCOMe)_n$ *(n=1-3)*

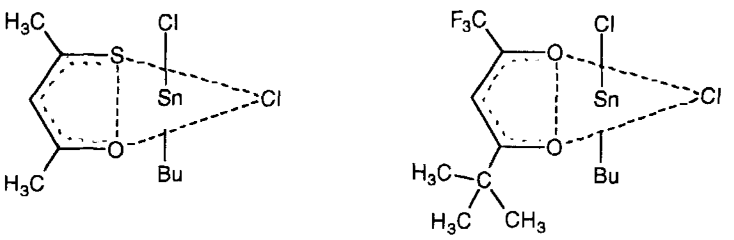
The IR spectral data of butyltin(IV) complexes with monothioacetylacetone, $BuSnCl_{3-n}(MeCSCHCOMe)_n$ (n = 1-3) are very helpful in understanding the mode of bonding of the ligands. In all monothioacetylacetonates of butyltin(IV), the decrease in the frequencies of ν(C=O) and ν(C=C) were observed at 1605 – 1580 cm^{-1} and 1500 – 1470 cm^{-1}, respectively consistent with bidentate behavior of the ligand.[11],[12] An intense band at 1225 – 1215 cm^{-1} (which occurs in the free ligand at 1245 cm^{-1}) has been assigned to ν(C=S) coupled with the ν(C=C) stretching mode of a system (S=C=C=C) which is quite possible for the chelate containing resonating double bonds in the ring.[13] Another observed band at 825 – 805 is due to ν(C=S) absorption coupled with δ(C-H). The intense band at about 500 cm^{-1} is due to the (Sn-C) stretching vibration.[14] A band due to the ν(Sn-O) vibration[15] appears in the region 475 – 460 cm^{-1} in all the complexes. The far IR region is characterized by a (Sn-S) mode[16] in the region 395 – 360 cm^{-1}. In addition, the chloro complexes exhibit a ν(Sn-Cl) vibration[17] between 342 – 290 cm^{-1}. The presence of two ν(Sn-Cl) vibration modes in $BuSnCl_2(MeCSCHCOMe)$ suggests the presence of two types of (Sn-Cl) stretching vibrations.

NMR spectra of $BuSnCl_{3-n}(MeCSCHCOMe)_n$ *(n = 1-3)*

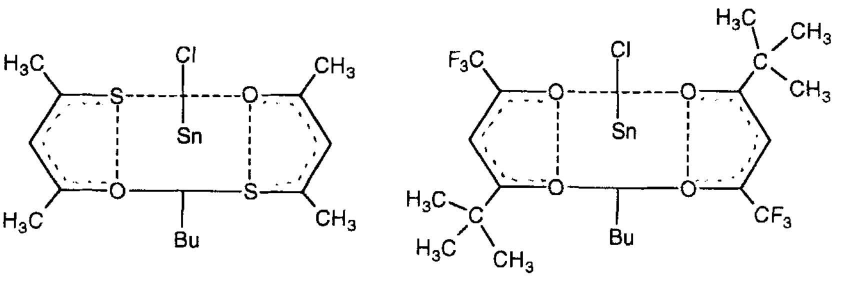
The ^1H and ^{13}C NMR data shed some light on the stereochemistry of monothioacetylacetonates of butyltin(IV). In the PMR spectra, mono, bis and tris complexes, $BuSnCl_{3-n}(MeCSCHCOMe)_n$ (n = 1-3), exhibit singlets for (S)-Me, (O)-Me and -CH= protons. These data, while consistent with the *trans*-octahedral structure for $BuSnCl(MeCSCHCOMe)_2$, can also be interpreted by *cis*-configurations undergoing fast exchange on the NMR time scale as observed for the acetylacetone analogue.[18] In the ^{13}C NMR spectra of all monothioacetylacetonates with butyltin(IV), $BuSnCl_{3-n}(MeCSCHCOMe)_n$ (n = 1-3), five resonances are observed for the ligand carbons. CO and CS carbon resonances shift in the downfield region suggesting bidentate coordination. The downfield shift is also seen for the methine carbon in all of the complexes. The most shielded methyl carbons attached to CS and CO come in the upfield region. A ^{119}Sn NMR spectrum of $BuSnCl_2(MeCSCHCOMe)$ confirms the coordination number five around tin.[19] The observed signal due to ^{119}Sn was found at −130 ppm. The presence of more than one ν(Sn-Cl) absorption may indicate a trigonal bipyramidal structure (Figure 1, I) with Bu and Cl groups occupying the axial position. Coordination number six[20] has also been confirmed around the tin atom in $BuSnCl(MeCSCHCOMe)_2$ by ^{119}Sn NMR data which show a signal at −235 ppm. Based on IR and NMR spectral data a *trans*-octahedral structure is proposed (Figure 1, III) for $BuSnCl(MeCSCHCOMe)_2$.

IR spectra of $BuSnCl_{3-n}(CF_3COCHCO^t\text{-}Bu)_n$ *(n = 1-3)*

The infrared spectra of mono, bis and tris complexes of butyltin(IV) with *tert*-butyltrifluoroacetylacetone, $BuSnCl_{3-n}(CF_3COCHCO^t\text{-}Bu)_n$ (n = 1-3), do not show any important band above 1615 cm^{-1}. The absence of bands above 1615 cm^{-1} in all of the complexes indicates that the ligands are coordinating to tin(IV) through both the oxygen atoms. Two strong bands in the region 1610 − 1580



I $[BuSnCl_2(CH_3CSCHCOCH_3)]$ II $[BuSnCl_2(CF_3COCHCO^t\text{-}Bu)]$



III $[BuSnCl(CH_3CSCHCOCH_3)_2]$ IV $[BuSnCl(CF_3COCHCO^t\text{-}Bu)_2]$

FIGURE 1 Proposed structure for the complexes of butyltin(IV) with monothioacetylacetone and *tert*-butyltrifluoroacetylacetone

cm^{-1} and 1525 – 1460 cm^{-1} are due to ν(C=O) and ν(C=C) vibrations,[21] respectively. The single absorption due to ν(Sn-C) vibration[22] in all of the complexes appears at 581 cm^{-1} while the (Sn-O) stretching vibration[11] appears in the region 430 → 415 cm^{-1}. In the chloro complexes the bands appearing below 400 cm^{-1} arise from (Sn-Cl) stretching vibrations.[13]

NMR spectra of $BuSnCl_{3-n}(CF_3COCHCO^t\text{-}Bu)_n$ *(n = 1-3)*

^1H NMR spectra of $BuSnCl_{3-n}(CF_3COCHCO^t\text{-}Bu)_n$ (n = 1-3), display a single peak for each of the *tert*-butyl and CH protons. In ^{13}C NMR spectra the carbonyl carbon attached to the *tert*-butyl group has a larger chemical shift in comparison to the carbonyl carbon containing the CF_3 group. $BuSnCl_2(CF_3COCHCO^t\text{-}Bu)$ has been examined by ^{119}Sn NMR. The value of −133.5 ppm provides a strong evidence for a coordination number[19] of five around the tin(IV). Since the compound has been considered to have a trigonal bipyramidal structure, the presence of two absorption bands due to ν(Sn-Cl) in the IR spectrum are consistent with the proposed structure (Figure 1, II). For $BuSnCl(CF_3COCHCO^t\text{-}Bu)_2$, which has much lower symmetry, several isomers are possible. In the ^{19}F NMR spectra from 24 to −60°C a singlet was observed at 74 ppm. ^{119}Sn NMR spectrum shows a singlet at −230 ppm confirming the coordination number six[20] around tin(IV). Based on spectral evidence a *trans*-octahedral structure (Figure 1, IV) is proposed for $BuSnCl(CF_3COCHCO^t\text{-}Bu)_2$.

Several isomers are possible around any geometrical configuration of $BuSn(MeCSCHCOMe)_3$ and $BuSn(CF_3COCHCO^t\text{-}Bu)_3$. Based on spectral data a pentagonal bipyramidal structure has been tentatively assigned for them because all three ligands are coordinating in a bidentate fashion to tin in both the cases. Attempts to grow single crystals of $BuSn(MeCSCHCOMe)_3$ with several solvent combinations at low temperature have been unsuccessful.

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